

PHOTOEMISSION FROM Au AND Cu INTO CdS

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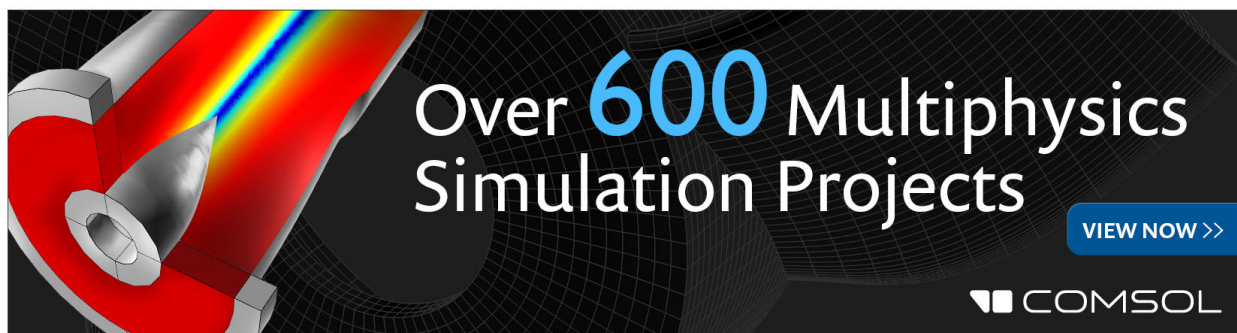
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PHOTOEMISSION FROM Au AND Cu INTO CdS

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Many metal-semiconductor surface barrier rectifiers show photosensitivity for photon energies ($h\nu$) less than the semiconductor energy gap (E_g). Cases in the literature¹⁻⁵ include metals evaporated or electrodeposited on elemental and III-V compound semiconductor surfaces. In these studies the source of the low-energy photocurrent, when $h\nu < E_g$, was shown to be the photoemission of carriers over the Schottky barrier between the metal film and the semiconductor. An extensive investigation has been reported⁶ for a series of metals, particularly Cu and Au, electroplated on *n*-type CdS with the conclusion that here also photoemission from the metal is responsible for most of the low-energy photovoltage. However, recent studies have questioned this conclusion for the CdS case. One study⁷ proposed that the origin of the low-energy photovoltaic response is electron photoexcitation from Cu impurities located in the CdS and within a diffusion length of the space charge region. Hole conduction probably in the 3^d Cu levels was postulated for these samples, which had ≈ 30 -ppm Cu. A second study⁸ interpreted the results as a *p-n* junction photovoltaic effect.

In these CdS studies, the surface was exposed to atmosphere (and, in some cases, a plating solution as well) prior to the deposition of the metal film. The spectral dependence of the photoresponse was qualitatively different from that obtained with the elemental and III-V semiconductors. It is known that a surface barrier rectifier may be sensitive to changes in the interfacial conditions.⁴ The introduction of a surface layer and surface states⁹

can alter the effective barrier height and photosensitivity.

In the present study, samples were prepared by cleavage of *n*-type CdS in an evaporating metal stream in high vacuum. The results obtained are similar to those for other metal-semiconductor systems and the low-energy response is directly attributable to photoemission from the metal.

Samples of the wurtzite structure, approximately 2 mm², parallel to the optic axis were cleaved in the stream of evaporating Au or Cu. Pressures were typically 5×10^{-8} Torr before evaporating and never rose above 10^{-6} during evaporation. Contact to the CdS was made with In solder and to the metal layer with a Au-wire probe. V-A characteristics showed all units to be good rectifiers.

The barrier height of each sample was determined from two measurements: capacitance vs voltage, and photo-threshold. A typical capacitance plot is shown in Fig. 1. The voltage intercept corresponds

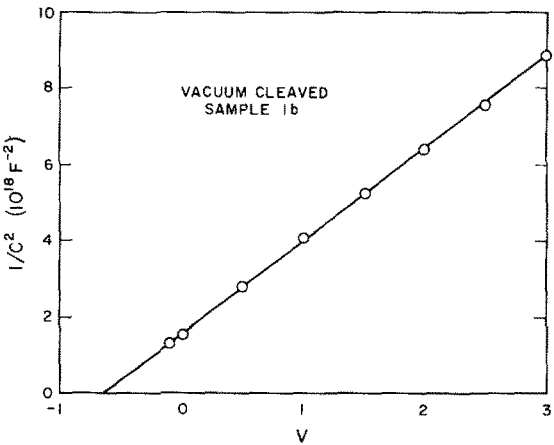


Fig. 1. Capacitance⁻² vs applied bias plot for a vacuum cleaved sample.

to the change in potential in crossing the depletion layer.¹⁰ To obtain the barrier height the difference (ΔE) between the Fermi level and the conduction band edge in the bulk semiconductor must be added.

INDEXING CATEGORIES	
A. compound (II-VI) semiconductors	B. Au, Cu photoemission
A. CdS	E
B. low-energy photo-voltaic effect	

The slope of this plot can be used to obtain the electron density and, hence, ΔE . However, the accuracy is poor since the value depends upon the square of a difficult-to-measure sample area. In some cases ΔE was obtained from Hall measurements or was estimated from resistivity measurements by using an assumed electron mobility.

Photoresponse measurements were made with a chopped-light system with the radiation incident on the metalized surface (front wall configuration). A typical photovoltaic curve is shown in Fig. 2a. A standard Fowler plot of the low-energy data is given in Fig. 2b.

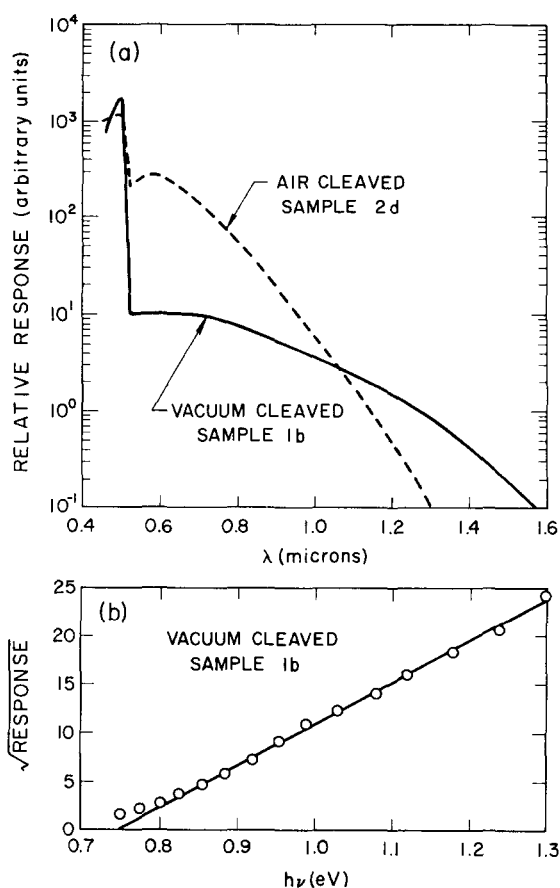


Fig. 2. a. Photoresponse per unit incident energy of vacuum cleaved and air cleaved samples; b. Square root of photoresponse per incident photon vs photon energy for vacuum cleaved sample. All vertical scales are in arbitrary units.

Data were taken on 9 Au and 3 Cu samples. The photovoltaic barrier and the $1/C^2$ barrier are in

reasonable agreement, in most cases within .05 eV. Although the metal thickness varies considerably between samples, the internal consistency of the data for both the Au and Cu cases is quite good. The barrier height (photo) for Au samples is 0.77 ± 0.02 eV and for Cu is 0.36 ± 0.02 eV. These data are in agreement with the hypothesis that photoemission from the metal is the dominant source of low-energy photoresponse of the samples cleaved in vacuum. In addition, mass spectrometer analysis showed the Cu content of the CdS to be $\lesssim 1$ ppm.

Data were taken on a number of samples cleaved in room air. After being exposed to air for several hours, some of the samples were etched in a dilute solution of HCL and HNO_3 before evaporating the metal film. These samples are generally much more photosensitive than vacuum cleaved ones. However, the consistency of the data is poor. Often the barrier heights obtained in the two measurements do not agree, $1/C^2$ barriers exceed 2 eV, the photoresponse does not obey a Fowler plot, and the $1/C^2$ vs voltage plot is not a straight line. The difference between the spectral response of vacuum cleaved and air cleaved samples with close to the same thicknesses of Au is illustrated in Fig. 2a. The air cleaved response curve is similar to those given in the literature for front wall cells and it appears that the behavior of these samples cannot be simply explained either on the basis of photoemission from the metal film or as photoexcitation of impurities originally present in the CdS crystal.

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